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Next 1 Page(s) In Document Denied

or Organophosphorus

Preparation of diphenyl phosphite.

A. E. Arbuzov and M. G. Imaev (G. M. Kirov Chem. Tech. Inst., Kazan).
Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 171.
Cf. Noack et al. Ann. 218, 92 (1883); Milobandzki et al., Chem. Polsk.
15, 66(1917); Kabachnik et al. Doklady Akad. Nauk SSSR, 115, 512 (1957).
$(PhO)_2HO$ may be prep'd. by careful hydrolysis of $(PhO)_3P$. Thus, 55 g.
$(PhO)_3P$ was treated with 3.25 g. H_2O and stirred 15-20 min. during which
the temp. rose to $85°$ spontaneously; after 1.5 hrs. on a steam bath the
resulting 15 g. PhOH was removed by vacuum distn. under N_2, leaving a
residue of 100% crude $(PhO)_2HO$, n_D^{20} 1.5590. This may be purified by
distn., although some PhOH and red P always forms during a distn.; the
pure product, 10 g., b_1 150-52$°$, n_D^{20} 1.5595, d_{20} 1.2396. It is very sen-
sitive to moisture.

...sters of β-oxophosphonic acids. 4. Infra-red spectra of the reaction products of γ-halo ketones with triethyl phosphite and diethyl sodiophosphite.

... . rbuzov and L. . Movsesyen. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 267-71. Cf. this J. 1957, 54, 1959, 41.

The infra-red absorption spectra are shown for the reaction products of appropriate γ-halo ketones with $(EtO)_3P$ or $(EtO)_2PONa$. The presence of the typical carbonyl band (5.84-5.85) indicates the normal ketonic structure of $MeCOCH_2PO(OEt)_2$ prepd. from the reaction with $(EtO)_3P$; the same is true of $MeCOCHMePO(OEt)_2$ and $EtCOCH_2PO(OEt)_2$ prepd. by the similar route. The reaction products of $AcCH_2Br$ and $MeCOCHBrMe$ with $(EtO)_2PONa$, on the other hand, do not display the carbonyl band and do show the epoxy band at 11.80-11.98 , thus indicating their structures as being those of epoxy phosphonates. The spectra do not provide sufficient basis for estn. of any enolization of the oxophosphonates, since the expected FOH band at 3.7-4 was unobservable. The spectra were detd. with solns. of the esters in CCl_4, hexane, EtOH and without solvents.

Organophosphorus

Organophosphorus

Diethyl ester of cyclohexanone-2-phosphonic acid.

B. A. Arbuzov, V. S. Vinogradova and N. A. Polezhaeva (State Univ., Kazan). Doklady Akad. Nauk S.S.S.R. 128, 81-4(1959).

Reaction of 2-chloro- or -bromocyclohexanone with $(RO)_3P$ yields the dialkyl cyclohexenyl phosphate. The reaction of bromocyclohexanone with $(RO)_2PONa$ yields the same product and dialkyl 1,2-epoxycyclohexanephosphonate. However, dropwise addn. of 52 g. $(EtO)_3P$ to 40 g. 2,6-dibromocyclohexanone, the reaction being completed by 1 hr. at 150-5° and 1 hr. at 185-90°, gave 27.6 g. EtBr and a range of products, $b_{2.5}$ 48-172°, which on redistn. gave 16.7 g. di-Et 6-diethylphosphono-Δ^{1-2}-cyclohexenyl phosphate (I), $b_{2.5}$ 172.5-3°, d_0^{20} 1.1885, n_D^{20} 1.4652. This (12.7 g.) refluxed 2 hrs. with 0.3 g. Na dissolved in 30 ml. abs. EtOH gave after neutralization with AcOH some $(EtO)_3PO$ and 3.5 g. di-Et 2-cyclohexanonephosphonate, $b_{3.5}$ 119-21°, 1.1258, 1.4654; its MR lies between 57.06 calcd. for the oxo form and 58.1 calcd. for the enol form. It gives a violet color with $FeCl_3$ and the Meyer bromination-titration indicated some 9% enol in EtOH and 60% enol in hexane. The Raman spectrum (242(1), 272(1), 337(2), 285(1), 446(1), 479(2), 525(1), 602(3), 658(5), 707(2), 753(2), 792(2), 824(3), 852(5), 900(0), 958(4), 986 (0), 1025(3), 1033(0), 1078(1), 1101(3), 1119(2), 1135(2), 1180(4), 1225(1), 1246(1), 1282(2), 1356(2), 1396(1), 1422(6), 1451(7), 1651(7), 1662(0), 1711 (3), 2720(2), 2767(0), 2867(5), 2900(3), 2934(6), 2975(4) cm^{-1}) indicates the presence of the keto form (1711) and the C:C bond of the enol (1671); the presence of both forms was also shown by the ultraviolet spectrum with maxima at 280 m and 220 m . In basic soln. a max. at 250 m appears due to formation of the enolate ions. I has the Raman spectrum: 645(0), 703(1), 748(2), 805(1), 850(0), 940(0), 1040(0), 1099(3), 1174(0), 1225(1), 1280(1), 1393(0), 1443(3), 1675(3), 2720(1), 2870(3), 2899(2), 2931(5), 2978(5) and 3054(0) cm^{-1}. Cf. Pudovik et al. Zhur.Obsh.Khim.26,1431(1956); Jacobson et al. JACS 79, 2608(1957).

Addition of phenylphosphine to unsaturated compounds.

B. A. Arbuzov, G. M. Vinokurova and I. A. Perfil'ova (Inst. Org. Chem., Acad. Sci., Kazan). Doklady Akad. Nauk S.S.S.R. 127, 1217-20 (1959). cf. Mann et al. J.C.S. 1952, 4453, and Doak and Freedman, JACS 74, 3414(1952) and 74, 562(1952).

Heating 13.5 g. $CH_2:CHCO_2Me$ and 6.2 g. $PhPH_2$ 6 hrs. at 120-30° gave 55.5% $PhP(CH_2CH_2CO_2Me)_2$, b_1 149-50°, d_{20} 1.1388, n_D^{20} 1.5361. Similarly were prepd.: 56.6% $PhP(CH_2CHMeCO_2Me)_2$, $b_{1.5}$ 139-40°, 1.1016, 1.5242; 57.8% $PhP(CH_2CHMe-CO_2Et)_2$, b_1 150-1°, 1.0764, 1.5172; 64.6% $PhP(CH_2CHMeCO_2Pr)_2$, b_1 170-1°, 1.0394, 1.5061; 65.7% $PhP(CH_2CHMeCO_2CHMe_2)_2$, b_1 152-3°, 1.0394, 1.5038; 66.9% $PhP(CH_2CHMeCO_2Bu)_2$, b_1 185-6°, 1.0267, 1.5038; 76.1% $PhP(CH_2CHMeCO_2-CH_2CHMe_2)_2$, b_1 178-9°, 1.0181, 1.5001; 56.16% $PhP(CH_2CH_2CH_2OH)_2$, b_1 175°, 1.1017, 1.5740 (the reaction used allyl alc. and a little $(Me_2C(CN)N:)_2$ initiator, 7 hrs. at 120-30°); reaction of 30.1 g. $PhPH_2$ and 49 g. $CH_2:CHCN$ in 3 hrs. at 90° and 6 hrs. at 120-30° gave 48.8% $PhP(CH_2CH_2CN)_2$, $b_{0.5}$ 176.5-8°, 1.1043, 1.5672 (m. 69-70°) and 7.9% $PhPHCH_2CH_2CN$, $b_{0.5}$ 104°, 1.0710 1.5649, along with 2.04% $PhP(O)(CH_2CH_2CN)_2$, m. 104-5°, $b_{0.5}$ 235-40°. Reduction of 10 g. $PhP(CH_2CH_2CN)_2$ with 7.2 g. $LiAlH_4$ in Et_2O, the phosphine being held in a Sohxlet thimble above the mixt., gave 48.5% $PhP(CH_2CH_2CH_2NH_2)_2$, b_1 144°, 1.0292, 1.5728. Addn. of atm. O or heating with S gave the following oxides and sulfides: 73.3% $PhP(S)(CH_2CHMeCO_2Me)_2$, $b_{0.5}$ 184°, 1.1712, 1.5495; 17.1% $PhP(O)(CH_2CHMeCO_2Et)_2$, b_1 177-8°, 1.1128, 1.5123; 18.2% $PhP(O)(CH_2CHMeCO_2Pr)_2$, $b_{0.5}$ 182-3°, 1.0686, 1.5028; 75.3% $PhP(S)(CH_2CHMe-CO_2Bu)_2$, $b_{0.5}$ 205-270°(???), 1.0789, 1.5219.

X Organophosphorus

Esters of phosphoric and thiophosphoric acid containing heterocyclic radicals. 2. Alkylation of some heterocyclic compounds by derivatives of phosphoric and phosphorous acids.

B. A. Arbuzov and Y. M. Zoroastrova (State Univ., Kazan). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1037-40 (1959). cf. 1958, 1331, and Zhur. Obshchei Khim. 22, 2041(1952).

Heating 41.5 g. K salt of 4,6,6-trimethyl-6H-1,3-thiazine-2-thiol suspended in C_6H_6 with 33.88 g. $(EtO)_2POCl$ 5 hrs. gave a reddish soln. with a small amt. of KCl; after centrifuging, the soln. was distd. yielding 45.8% ethylation product of 4,6,6-trimethyl-6H-1,3-thiazine-2-thiol, $C_9H_{15}S_2N$, b_3 91-2°, d_0^{20} 1.0497, n_D^{20} 1.5518; the same formed from the above K salt and EtI in refluxing C_6H_6. Similar reaction of the K salt with $(iso-BuO)_2$-POCl gave a low yield of crude 4,6,6,-trimethyl-6H-1,3-thiazine-2-thiol iso-Bu ether, $b_{3-3.5}$ 99-101°, n_D^{20} 1.5370, d_0^{20} 1.0032. Refluxing 9.45 g. K salt of 2-mercaptobenzoxazole with 8.6 g. $(EtO)_2POCl$ in dry Me_2CO 5 hrs. gave after centrifuging 64.7% 2-ethylmercaptobenzoxazole, $b_{4.5-5}$ 114-15° (I), d_0^{20} 1.1837, n_D^{30} 1.5940. Oxidation of 2-mercaptobenzoxazole with 5% H_2O_2 in AcOH at 3-6° gave benzoxazole-2 disulfide, m. 112-3°. This treated with 2 moles $(EtO)_3P$ in xylene gave an exothermic reaction, completed by 1 hr. on a steam bath, which gave 77.4% I. The above disulfide was treated with Cl_2 in MePh at -15° and the resulting sulfenyl chloride was treated with $(EtO)_3P$ at -10°, yielding 36% I. Reaction of K salt of 2-mercaptobenzothiazole with $(EtO)_2POCl$ in MePh gave 72% 2-ethylmercaptobenzothiazole, the same being formed in 83.7% yield from benzothiazole-2 disulfide and $(EtO)_3P$ or $EtOP(OCH_2)_2$ (41.3% yield).

Organophosphorus

Action of halo-substituted ethers on salts of dialkyl phosphites.
A.E.Arbuzov and V.S.Abramov (Chem. Technol.Inst., Kazan). Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 35-40.

Reaction of $(EtO)_2PONa$ from 13.5 g. ester and 2.2 g. Na, in Et_2O with 12.5 g. $MeOCH_2Br$ rapidly gave 100% NaBr and 70% $MeOCH_2P(O)(OEt)_2$, b_2 102-104°, n_D^{20} 1.4250, d_{15}^{15} 1.096. If the NaBr is not sepd. for distn. of the product, the latter reacts and dissolves it during distn. at about 200° bath temp. in an exothermic reaction which evolved gaseous products; on cooling, the mixture solidified and after pptn. from EtOH with Et_2O the product was shown to be $MeOCH_2P(O)(ONa)OEt$, m. 176-77°. Reaction of $(EtO)_2PONa$ from 13 g. ester and 2.2 g. Na in Et_2O, with 9.5 g. $MeOCH_2Cl$ was quite slow and gave mixture $MeOCH_2P(O)(OEt)_2$ along with some $(EtO)_3P$. To a soln. of $(EtO)_2PONa$ in Et_2O, contg. 0.15 g. Na, was added 2.5 g. $(PhO)_3P.CuBr$ adduct after which 0.5 g. $MeOCH_2Cl$ was added and the whole heated briefly; the pptd. NaCl was sepd. and the filtrate on evapn. gave only $(PhO)_3P$-CuBr adduct. $(MeO)_2PONa$ and $MeOCH_2Br$ in Et_2O gave 40% $MeOCH_2P(O)(OMe)_2$, b_7 91-2°, n_D^{20} 1.4242. Use of $MeOCH_2Cl$ gave unstated yield of the same product, b_7 91-1.5°, n_D^{20} 1.4242, d_0^{18} 1.1898. Heating 11 g. $(MeO)_2POAg$ and 6.5 g. $MeOCH_2Br$ in C_6H_6 resulted in soln. of the Ag salt, followed by pptn. of 8 g. AgBr; distn. gave unstated yield of $MeOCH_2P(O)(OMe)_2$, b_7 91-2°, 1.4242, 1.1899 and a little AgBr residue. If the solvent is carefully distd. from the reaction mixture, the viscous residue is an adduct which yields AgBr at 110-15°. Reaction of 20 g. $(EtO)_2POAg$ and 6.6 g. $MeOCH_2Cl$ in C_6H_6 gave some free Ag and a ppt.; the yellow soln. was decanted and distd. yielding a residue of 12 g. AgCl, 2.7 g. $(EtO)_3P$, and 4 g. product, b_9 46-48°, which gave an exothermic reaction with CuX but failed to give a solid adduct. Reaction of $(BuO)_2POAg$ with $MeOCH_2Cl$ gave crude mixed esters of H_3PO_3 (test with CuI): b_{10} 80-115°, a product, b_{10} 115-20°, and AgCl. To 2.6 g. $(EtO)_2POAg$ in C_6H_6 was added 1.5 g. $MeOCH_2Br$, the mixture was heated until the ppt. had dissolved, and the soln. decanted from the ppt. was treated with 2 g. $PhCOBr$ yielding 1.5 g. AgBr and an oil, which heated with MeI

8

in a sealed tube gave Ph_3COH. Similarly, the use of $MeOCH_2Cl$ gave $AgCl$ and an unpirifiable mass which with HCl gave $Ph_3CP(O)(OH)_2$, m. 270-72°. Addn. of 1 g. Ph_3CBr in C_6H_6 to 1 g. of adduct of $AgBr$ and $(EtO)_3P$ gave after heating, some $AgBr$ and a liquid which on comen. gave $Ph_3CP(O)(OEt)_2$, m. 120-21°. Ph_3CBr reacts with $(EtO)_3P$ in hot C_6H_6 and gives the same ester. Evidently, $MeOCH_2Cl$ tends to yield mixed esters of H_3PO_3.

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Esters of β-keto phosphonic acids. 3. Structure of reaction products of some halogenated ketones with triethyl phosphite and sodium diethyl phosphite.

B.A.Arbuzov, V.S.Vinogradova and N.A.Polezhaeva (State Univ., Kazan). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 41-49. Cf. Doklady Akad. Nauk SSSR, 99, 85 (1954), 106, 263 (1956), 106, 465 (1956), 111, 107 (1956), and this j. 1957, 54 and 284.

Reaction of 46.8 g. (EtO)$_2$PHO with 7.4 g. Na in Et$_2$O gave the Na salt which was slowly treated with 30 g. MeCOCH$_2$Cl at b.pt. of the solvent; after heating on a steam bath, the NaCl was sepd. by centrifuging, and the product was distd. yielding 18 g. (EtO)$_2$P(O)CMeCH$_2$O, b$_2$ 91°, n$_D^{20}$1.4517, d$_o^{20}$1.1154, (I)
and 9 g. (EtO)$_2$P(O)CH$_2$Ac, b$_{1.5}$ 101-103°, 1.4348, 1.1115, which gave a (II)
2,4-dinitrophenylhydrazone, m. 104-105° (cf.Kreutzkamp and Kayser, Ber, 89, 1614 (1956); present authors could not duplicate the isolation of the isopropenyl ester described by these authors). Similar reaction of (EtO)$_2$-PONa from 36 g. (EtO)$_2$PHO in Et$_2$O with 34.2 g. BrCH$_2$COMe gave unstated yield of I, b$_{9.5}$ 111°, 1.4313, 1.1141, and II, b$_{3.5}$ 107-112°, 1.4347, 1.1119 which gave the dinitrophenylhydrazone, m. 104-105°. Carefully fractionated AcCH$_2$P(O)(OEt)$_2$, prepd. ~~wither~~ by the Arbuzov method ~~xxxxxxxxxxxxxxx~~ ~~xxxxxxy~~ was shown to be an individual substance with b$_5$ 109°, d$_o^{20}$ 1.1153, n$_D^{20}$1.4346. The similar product prepd. with (EtO)$_2$PONa had b$_{2.5}$ 86°, 1.1152, 1.4317, which was actually I rather than II. Itsformation may be explained by reaction of the Na salt at the carbonyl group rather than at the Br atom. The Raman spectrum of I is (in cm^{-1}): 285(5), 326(3), 463(3), 527(1), 627(2), 638(4), 749(4), 796(4), 810(2), 851(4), 923(3), 995(2), 1027(1), 1069(1), 1100(4), 1160(2), 1217(3), 1266(3), 1290(2), 1350(6), 1381(2), 1397(2), 1452(7), 1478(2), 2725(1), 2870(2), 2904(3), 2932(5), 2963(4), 3061(1). The C:O and C:C lines are absent and the 1266 line of epoxy ring is present. This spectrum was the same as that produced by the I prepd. by dehydrochlorination of ClCH$_2$CMe(OH)P(O)(OEt)$_2$. Reaction of AcCH$_2$Br

with $(EtO)_3P$ gave I and $(EtO)_2P(O)OCMe:CH_2$, whose Raman spectrum was:
299(1), 470(1), 521(0), 707(5), 751(2), 814(1), 860(1), 911(1), 1054(3),
1070(1), 1100(3), 1162(1), 1289(4), 1371(3), 1397(4), 1447(3), 1457(3),
1478(1), 1662(6), 2729(2), 2870(3), 2901(2), 2931(6), 2974(5), 3003(4),
which is rather similar to that of Et_3PO_4 but has the C:C line
at 1662. Raman spectrum of II is: 237(3), 268(3), 323(2), 455(3), 532(2),
593(3), 667(0), 718(6), 768(1), 791(1), 819(3), 851(2), 961(1), 1028(2),
1101(5), 1128(1), 1165(1), 1200(1), 1257(5), 1293(3), 1368(1), 1396(3),
1425(1), 1451(5), 1480(2), 1658(1), 1715(4), 2725(2), 2775(2), 2872(4),
2900(5), 2926(8), 2973(6), 3000(2). Reaction of $(iso-PrO)_2POMe$ and $ClCH_2Ac$
gave $(iso-PrO)_2P(O)CMeCH_2O$, $b_{3.5}$ 94°, d_0^{20} 1.1154, n_D^{20} 1.4317; use of
$BrCH_2Ac$ gave the same epoxy deriv. $b_{9.5}$ 111°, 1.1141, 1.4313. In both
cases some $(iso-PrO)_2P(O)CH_2Ac$ was formed, $b_{1.3}$ 101-103°, 1.1115, 1.4343.
Reaction product of $(EtO)_3P$ with $EtCOCH_2Br$ is evidently an ester of -keto-
butylphosphonic acid with Raman spectrum: 265(2), 324(2), 405(1), 455(2),
553(1), 614(1), 658(1), 711(7), 793(4), 820(3), 867(2), 949(2), 1028(5),
1054(2), 1101(6), 1164(1), 1200(1), 1256(5), 1290(4), 1363(2), 1405(5),
1453(6), 1477(4), 1654(1), 1715(6), 2725(2), 2768(1), 2875(3), 2903(5),
2936(8), 2978(6). Methylation of K deriv. of II or its Me deriv. yields
products which have the structure of II: mono-Me deriv. has the Raman
spectrum 297(3), 412(2), 504(1), 614(3), 652(2), 694(4), 709(2), 751(2),
794(2), 813(3), 941(0), 969(0), 1024(0), 1059(1), 1098(4), 1164(1), 1208(1),
1249(1), 1289(2), 1395(1), 1451(1), 1712(5), 2901(2), 2932(5), 2978(3),
and the di-Me deriv.: 295(2), 357(2), 458(1), 570(1), 598(10), 654(5), 695
(2), 744(2), 791(3), 808(2), 899(3), 960(3), 1025(2), 1099(4), 1184(1),
1163(2), 1247(3), 1291(2), 1366(2), 1390(2), 1453(5), 1473(2), 1707(3),
2876(2), 2908(1), 2930(3), 2980(4). The reaction product of $(EtO)_2POMe$
with MeCOCHMe lacks the C:O line in the spectrum and that of C:C, which
indicates that the substance is an epoxy deriv., ester of epoxyisobutyl-
phosphonic acid. Its Raman spectrum is: 284(3), 332(3), 476(3), 508(1),

8

541(2), 655(2), 647(5), 741(7), 770(1), 796(1), 812(1), 858(5), 909(4), 948(1), 989(2), 1028(5), 1069(0), 1100(7), 1115(2), 1146(1), 1165(1), 1205 (2), 1261(5), 1289(2), 1301(5), 1370(1), 1395(1), 1415(5), 1452(6), 1479(2), 2720(1), 2769(1), 2871(4), 2905(5), 2934(6), 2960(5), 5005(5), 5061(1). This does not form a dinitrophenylhydrazone. Me deriv. of authentic II gives 2,4-dinitrophenylhydrazone, m. 110-15°. Reaction product of MeCOCHrMe₂ and (EtO)₂PONa or (EtO)₃P is not too well characterized by Raman spectra as both products gave C:O bands that were displaced from normal (1699 and 1700 instead of 1707 cm⁻¹). The di-Me deriv. of II prepared by Arbuzov reaction had the Raman spectrum: 382(1), 511(1), 548(2), 579(4), 689(6), 749(5), 812 (2), 857(1), 965(2), 1011(5), 1035(2), 1066(1), 1160(5), 1165(1), 1236(4), 1376(2), 1394(4), 1450(6), 1475(1), 1699(5), 2452(0), 2724(2), 2777(2), 2865 (4), 2905(2), 2932(5), 2981(5), 5004(2). The di-Me deriv. of I prepd. via the Na salt of the ester had Raman spectrum: 256(5), 334(2), 397(1), 479(2), 521(5), 548(1), 577(5), 631(5), 653(1), 686(6), 751(5), 796(2), 815(4), 868 (5), 946(2), 975(5), 1024(5), 1058(0), 1099(6), 1164(1), 1230(5), 1261(1), 1285(4), 1356(4), 1378(1), 1591(5), 1451(7), 1480(4), 1700(6), 2455(1), 2730 (2), 2773(1), 2868(4), 2903(4), 2929(6), 2976(4), 5006(2), 5055(2). The absorption spectrum of III is different from that of di-Me deriv. of II prepd. by methylation of II; III lacks the carbonyl group band. The true structure of III remains unclear. Reaction of (EtO)₂PONa with MeCOCH₂CH₂Cl failed to yield the expected product since undistillable products formed either through polymerization of the possible vinyl ketone or for other reasons. The reaction with MeCO(CH₂)₃Cl gave a good yield of a product with b₃.₅ 108-10°, d₄²⁰ 1.0898, n_D²⁰ 1.4432; its Raman spectrum/has: 276(2), 504(2), 586(2), 614(4), 700(2), 723(6), 757(1), 792(5), 809(2), 836(4), 861(4), 911 (2), 927(6), 1003(4), 1054(4), 1099(6), 1159(4), 1204(4), 1244(5), 1285(2), 1295(5), 1355(2), 1368(5), 1451(6), 1480(5), 2725(1), 2773(0), 2869(5), 2906 (5), 2955(6), 2978(4), 3000(2), which agrees with formulation of di-Et 2-methyl-2-tetrahydrofuranphosphonate(cf. Arbuzov et al. Zhur.Obsh.Khim.20, 1448(1950) where the product was described as oxopentylphosphonate).

Action of triarylmethyl halides on silver salts of dialkyl phosphites.
A.E.Arbuzov and E.A.Krasil'nikova (Chem. Technol. Inst., Kazan). Izvest.
Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 30-34.

Reaction of $(RO)_2POAg$ with Ar_3CX was examined. $(MeEtCHO)_2PHO$, prepd. for
the first time, had b_{14} 103-104°, n_D^{20} 1.4190, d_e^{20} 0.9754. The Ag salts
were prepd. by previously described technique (Arbuzov, Selected Works,
Moscow, 1952). Heating 4.89 g. $(iso\text{-}PrO)_2POAg$ with 6.84 g. $o\text{-}ClC_6H_4CCl\text{-}$
$(C_6H_4Cl\text{-}p)_2$ in C_6H_6 0.5 hr. on a steam bath gave after filtration of AgCl,
(I)
reheating to boiling, filtration of addnl. AgCl, and evapn. 21.2%
$(iso\text{-}PrO)_2POC(C_6H_4Cl\text{-}o)(C_6H_4Cl\text{-}p)_2$, m. 128-29° (from petr. ether), which
with dil.HCl at 150° in 3 hrs. gave Ar_3CCH. Ag salts of Et, iso-Bu, iso-Pr
and sec-butyl phosphites react similarly with Ar_3CCl and yield the mixed
esters of H_3PO_3, i.e. $(RO)_2POAr$ Ag salts of phosphites with primary radi-
cals (except the Et noted above) react with Ar_3CBr and yield esters of
phosphonic acids. These were also prepd. for comparison from $(RO)_3P$ and
the desired halide. The following are reported: $(EtO)_2P(O)C(C_6H_4Cl\text{-}o)(C_6\text{-}$
$H_4Cl\text{-}p)_2$, m. 116-17°; $(EtO)_2P(O)C(C_6H_4Me\text{-}p)_3$, m. 127-29°; $(iso\text{-}PrO)_2P(O)\text{-}$
$C(C_6H_4Cl\text{-}o)(C_6H_4Cl\text{-}p)_2$, m. 190-91°; $(iso\text{-}PrO)_2P(O)C(C_6H_4Me\text{-}p)_3$, m. 108-10°;
$(MeEtCHO)_2P(O)C(C_6H_4Cl\text{-}o)(C_6H_4Cl\text{-}p)_2$, m. 110-11°; $(iso\text{-}BuO)_2P(O)C(C_6H_4Cl\text{-}o)\text{-}$
$(C_6H_4Cl\text{-}p)_2$, m. 107-108°; $(iso\text{-}BuO)_2P(O)C(C_6H_4Me\text{-}p)_3$, m. 94-96°. If the
Ag salt of the phosphite contains secondary alkyl groups, the reaction with
Ar_3CBr yields $(RO)_2POAr$, i.e. an ester of H_3PO_3. Reaction without heating
gives the same results as one with heating; keeping a sealed tube with
$(EtO)_2POAg$ and I 15 days in Et_2O gave the oily phosphite ester which with
HCl readily gave H_3PO_3 and the arylcarbinol. Cl in the aryl group of
triarylmethyl halide tends to yield the mixed phosphite esters, while Me
substituent tends to produce phosphonate esters; in this case either
triarylmethyl chloride or bromide gave the same results in boiling C_6H_6.
The mixed phosphites were thick undistillable oils and their formation
was established only indirectly. The phosphonates, on the other hand, were
readily crystallizable solids.

Organophosphorus

Reaction of phosgene and oxalyl chloride with esters of phosphorous acid.
A. N. Pudovik and R. N. Platonova (State Univ., Kazan). Zhur. Obshchei Khim.
29, 507-10 (1959). Cf. Kabachnik et al., Izvest. Akad. Nauk SSSR, Otdel. Khim.
Nauk 1945, 364, 597; 1947, 163; and especially 1957, 48 and 1958, 1938.
Passage of dry $COCl_2$ through $(RO)_3P$, with or without water-cooling, or addn.
of $(RO)_3P$ to liq. $COCl_2$ cooled with a freezing mixt., followed by stirring
0.5 hr. and a vacuum distn. resulted in 60-70% $(RO)_2POCl$. The reaction was
run with specimens of $(RO)_3P$ in which R=Me, Et, Bu, or iso-Bu. Thus were
prepd. $(RO)_2POCl$: (R shown) Me b_9 64.5-5°, n_D^{20} 1.4119, d_{20} 1.3396; Et, b_8 78.5;
1.4180, 1.1989; Bu, b_{11} 120°, 1.4312, 1.0760; iso-Bu, b_8 110-10.5°, 1.4268,
1.0699. The products were identical with those formed by chlorination of
$(RO)_2PHO$. Evidently the reaction with $COCl_2$ yields the above chlorides along
with CO and RCl. To 30 g. $(COCl)_2$ in 100 ml. Et_2O there was added with cool-
ing 40 g. $(EtO)_3P$ and after 1 hr. on a steam bath, the mixt. yielded 12.7
g. $(EtO)_2POCl$. The reaction with $(MeO)_3P$ gave a similar result; this reaction
yields RCl and 2 moles of CO. Reaction of $(EtO)_3P$ with maleic chloride occurs
very violently and yields only tars even in solvents. Also cf. Baudler and
Griese, Z. allgem. anorg. Chem. 290, 258 (1957).

ddition of partial esters of phosphorus acids to nitroisoamylene and
ethyl vinyl sulfone.

. .. udovik and F. N. Gitdikova (State Univ., Kazan). Doklady Akad. Nauk
. . .S. 125, 826-8 (1959).

(RO)$_2$PHO add readily to Me$_2$CHCH:CHNO$_2$ in the presence of RONa catalyst and
cause considerable heat evolution. Thus were prepd. 56% Me$_2$CHCH(CH$_2$NO$_2$)P(O)-
(OMe)$_2$, b$_5$ 130°, n$_D^{20}$ 1.4505, d$_{20}$ 1.1740, and 37% Me$_2$CHCH(CH$_2$NO$_2$)P(O)(OEt)$_2$,
b$_4$ 144°, 1.4480, 1.1218. (RO)$_2$PHS was warmed with Et$_2$N and distd. directly
before the reaction which yielded 27% Me$_2$CHCH(CH$_2$NO$_2$)P(O)(OMe)$_2$, b$_9$ 121.5°,
1.4567, 1.1951. The reaction with EtO$_2$CCH$_2$PO(OEt)$_2$ required much RONa and
heating several hours at 100-10° in forming 40% (EtO)$_2$P(O)CH(CO$_2$Et)CH(CH$_2$NO$_2$)-
CHMe$_2$, b$_3$ 170°, 1.4372,-. Attempts to add (RO)$_2$PHO and (RO)$_2$PHS to nitrosty-
rene and furylnitroethylene, even in the presence of mild bases such as
piperidine or Et$_2$N, resulted in polymerization of the olefins and no adducts
could be isolated. Reaction of CH$_2$:CHSO$_2$Et with the above substances in
the presence of RONa gave: 70% (MeO)$_2$P(O)CH$_2$CH$_2$SO$_2$Et, b$_3$ 130°; 51% (EtO)$_2$P(O)-
CH$_2$CH$_2$SO$_2$Et, b$_{1.5}$ 154°, 1.4632, 1.2209; 34% (PrO)$_2$P(O)CH$_2$CH$_2$SO$_2$Et, b$_2$ 190°,
1.4526, 1.1523; 32% (BuO)$_2$P(O)CH$_2$CH$_2$SO$_2$Et, b$_3$ 208°, 1.4596, 1.1091; 46%
(EtO)$_2$P(S)CH$_2$CH$_2$SO$_2$Et, b$_2$ 182°. Also produced by similar addn. was 40%
(EtO)Et$_2$P(O)CH$_2$CH$_2$SO$_2$Et, b$_{2.5}$ 204°. The substances above for which only the
b.p. is listed, crystallized or solidified on standing (no m.p. cited).
Reaction of the sulfone with (EtO)$_2$P(O)CH$_2$CO$_2$Et proceeded so energetically
that only tar was formed.

C Organophosphorus

Reactions of aldehydes and ketones with amides of phosphorous acid esters. V. S. Abramov and M. A. Ilina (S. M. Kirov Chem. Technol. Inst., Kazan). Doklady Akad. Nauk S.S.S.R. 125, 1027-9 (1959).

Reaction of aldehydes and ketones with o-$C_6H_4O_2$PNHPh proceeds probably through an adduct of onium type, o-$C_6H_4O_2$P(NHPh)CHRO$^-$, which rearranges to the final product o-$C_6H_4O_2$P(O)(NHPh)CHRO. The reaction starts with mixing of the reactants and is exothermic. If no attempt to control the temp is made, the products are yellow; with careful mixing, the products remain colorless. Thus were prepd. o-C_6H_4OP(O)(NHPh)CHRO (R shown): Me, m. 145-6° (from dioxane); Et, m. 149.5-50.5° (from EtOH); Ph, m. 182-3° (from EtOH); Me$_2$, m. 173-4° (washed with starting material, Me$_2$CO); (CH$_2$)$_5$, m. 156-7° (from EtOH). Reaction with PhNH(OPh)$_2$ (cf. Kabachnik et al, this J. 96, 991(1954)) with BzH gave (PhO)(PhNH)P(O)CH(OPh)Ph, m. 149-50° (from EtOH); similarly cyclohexanone gave (PhO)(PhNH)P(O)C(OPh)(CH$_2$)$_5$, m. 157-8° (from EtOH). The structural formulas of the products are given provisional, on the assumption that a form of Arbuzov rearrangement is involved in the reaction. Hydrolysis of the products with dil.HCl yielded only catechol or PhOH and PhNH$_2$; no hydroxyphosphonic acids were isolated.

d Organophosphorus

Reaction of glyceral α,γ-dichlorohydrin with PCl_3, $POCl_3$ and $PSCl_3$.
B. V. Kuznetsov and R. K. Valetdinov (S. M. Kirov Chem. Tech. Inst., Kazan).
Zhur. Obshchei Khim. 29, 235-8 (1959). cf. Gosh et al. J. Chem. Soc. 1945,
873, and Jones et al. J. Chem. Soc. 1946, 824.

Addn. of 154.8 g. $HOCH(CH_2Cl)_2$ at 30° to 164.4 g. PCl_3, followed by stirring
1 hr. and a distn. gave a range of fractions which yielded: 44.9% $(ClCH_2)_2$-
CHOPCl$_2$, b_{12} 95-6°, d_{20} 1.5115, n_D^{20} 1.5310, 40.1% $[(ClCH_2)_2CHO]_2PCl$, $b_{0.2}$
126-7°, 1.4891, 1.5193, and 14.4% $[(ClCH_2)_2CHO]_2P(O)CH_2CHClCH_2Cl$, $b_{0.07}$
175-8°, 1.5010, 1.5135. The latter heated with concd. HCl 10 hrs. at 150°
and evapd. gave a crystalline Ba salt of the free acid $C_3H_5O_3PBaCl_2$. The
phosphonate evidently formed through internal isomerization of the expected
trialkyl phosphite. Treatment of 13.2 g. I in Me_2O with 0.73 g. H_2O and
3.2 g. pyridine at -5° gave after filtration and distn. 61.5% $[(ClCH_2)_2CHO]_2$-
PHO, $b_{0.4}$ 145-7°, 1.4865, 1.5010. Addn. of 25.8 g. $HOCH(CH_2Cl)_2$ at 100° to
30.6 g. $POCl_3$ and stirring 2.5 hrs. at 130° gave some 18 g. $(ClCH_2)_2CHO$-
$POCl_2$, b_{12} 122-4°, 1.5800, 1.4885, and some 10 g. $[(ClCH_2)_2CHO]_2POCl$, b_2
180-2° with decompn. (treated with $PhNH_2$ it gave the corresponding anilide,
m. 80-1°); the residual R_3PO_4 could not be distd. owing to decompn. Addn.
of 33.2 g. $(ClCH_2)_2CHOH$ to 42.5 g. boiling $PSCl_3$ and heating 1 hr. at 150°
gave a mixt. which failed to yield any definite products on distn.; only
some ill-smelling decompn. products were secured.

Addition of neutral esters of phosphorous and phosphinic acids to conjugated
systems. VII. Telomerisation of methacrylic acid with trialkyl phosphites.
V. A. Kukhtin, G. Kamai, L. A. Sinchenko and K. M. Orekhova (Chem. Technol.
Inst., Kazan). Zhur. Obshchei Khim. 29, 510-15 (1959). Cf. 28,1196(1958) and
28, 2790(1958). Also Connel and Coover, JACS 78, 4453 (1956).

Keeping 8.3 g. $(EtO)_3P$, 21.5 g. $CH_2:CMeCO_2H$ and 0.03 g. Bz_2O_2 3 hrs. at room
temp. gave 3.1 g. ppbd. telomer, augmented by 0.7 g. more formed overnight.
The product, a colorless solid was sol. only in warm EtOH or MeOH and AcOH.
Similarly were prepd. telomers of these monomers in various proportions with
Bz_2O_2, MeONa, iso-AmX or Et_3N catalysts, as well as telomers employing (Pr-
$O)_3P$, $(BuO)_3P$ and the initial adduct of $CH_2:CMeCO_2H$ and $(EtO)_3P$. These

2

telomers contained free CO_2H groups and could be titrated with base in the presence of phenolphthalein (this and the results of P analysis were used to est. the mol. wts. which ranged from a few hundred to approximately 200 The telomers did not have definite m. pts. but charred on being heated. In general the mol. wt of the telomers rose with increased proportion of the $CH_2:CMeCO_2H$ monomer and with increased concn. of the initiating catalysts. The tendency to enter the reaction among the phosphites declines with increasing mol. wt. of radical R. The reaction of $(EtO)_3P$ with $CH_2:CHCO_2H$ fails to yield any polymer and gave only the products of the Arbusov reaction. The results suggest that the original adduct (1:1) of the monomers which is evidently $(RO)_3\overset{+}{P}CH_2\overset{-}{C}MeCO_2H$, probably is the chain-initiating link in the telomerization. The mechanism of the reaction is discussed.

Organophosphorus

Addition of neutral esters of phosphorous acid to p-benzoquinone.
V. A. Kukhtin and K. M. Orekhova (All Union Cine-Photo Res. Inst., Kazan
Section). Doklady Akad. Nauk SSSR, 124, 619-21 (1959).
Cf. this j. 109, 91(1956); Zhur. Obshch. Khim. 27, 2372 (1957) and 28,
1196 (1958). Also, Ramirez et al. JACS 78, 5614(1956), J. Org. Chem. 22,
857(1957), 23, 778 (1958); Horner et al. Ber. 91, 58 (1958).
Gradual addn. of $(RO)_3P$ to a C_6H_6 soln. of p-benzoquinone with cooling
to 60-70° resulted in the products listed below. Acid hydrolysis of these
gave mainly hydroquinone; hydrolysis with aq. alc. base also resulted in
the loss of the P residue. These facts and the detection of a free phenolic
group in the products indicated that these are $2,5-(RO)(HO)C_6H_3P(O)(OR)_2$;
the following are described (R shown): R= Me, b_6 162-63°, n_D^{20} 1.4960, d^{20}
1.2423; Et, b_5 162-65°, 1.4870, 1.1531; Pr, b_2 175-76°, 1.4820, 1.1416.
The yields were 51-65%. These are not esters of phosphoric acid since the
reaction of $(EtO)_2POCl$ with p-HOC_6H_4OEt gave $(EtO)_2P(O)OC_6H_4OEt$-p, 72%,
b_3 150-51°, 1.4905, 1.1551, which differed from the material obtained by
the addn. of $(EtO)_3P$ to the quinone. It is possible however that the phos-
phono group may be located o- to the OH group rather than to OR group,
in the 3 products described above. It is suggested that the reaction goes
through an Arbuzov-type intermediate adduct with a possibly polar link
between P and the O-atom of the quinone, which then rearranges to the
phosphonate. $(PhO)_3P$ failed to react at room temp.; on heating in C_6H_6
a red color developed and a ppt. formed; this was a colorless solid which
turned to red tar in air and had a phenolic odor; it decomposed at 70-75°
yielding a red tar; abs. EtOH gave a red tar and a phenol. The liquid
portion of the mixture gave only some PhOH on distn. Analysis of the above
solid indicated that it is an Arbuzov-type adduct of $P(OPh)_3$ and p-benzo-
quinone; the 2nd phase of the Arbuzov reaction of this substance gave only
a tar. Paramagnetic resonance measurements during these reactions failed to
show the presence of radicals; diphenylpicrylhydrazyl also showed the
absence of radicals. Reaction of chloranil and $(EtO)_3P$ however displays
evidence of radicals.

Derivatives of γ**, -dichlorovinyl ester of ethylphosphonic acid.**
B. I. Rizpolozhenskii and M. A. Zvereva (A. E. Arbuzov Chem.Inst., Akad.
Sci., Kazan). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 358-60.
Cf. A.E.Arbuzov et al. this J. 1951, 531; 1952, 854; 1955, 1021.
Under CO_2 atm. 13.9 g. CCl_3CHO in 25 ml. C_6H_6 was treated dropwise with
11.5 g. $EtP(OMe)_2$ in 15 ml. C_6H_6 at -10°; after 1 hr. at room temp., the
mixture was refluxed 30-40 min. and distd. yielding 16 g. $EtP(O)(OMe)O-$
$CH:CCl_2$, $b_{0.5}$ 63-66°, d_{20} 1.3333, n_D^{20} 1.4680. Similarly were prepd.: 67.5%
$EtP(O)(OEt)OCH:CCl_2$, b_1 71-72°, 1.2734, 1.4637; 68% $EtP(O)(OPr)OCH:CCl_2$,
$b_{0.5}$ 83-86°, 1.2314, 1.4620; 73% $EtP(O)(OCHMe_2)OCH:CCl_2$, $b_{0.5}$ 73-74°,
1.2260, 1.4575; 68.5% $EtP(O)(OBu)OCH:CCl_2$, $b_{0.5}$ 92-95°, 1.2002, 1.4624;
73% $EtP(O)(OCH_2CHMe_2)OCH:CCl_2$, $b_{0.5}$ 89-90°, 1.1899, 1.4570; 70.5% $EtP(O)-$
$(OAm)OCH:CCl_2$, $b_{0.5}$ 100-101°, 1.1672, 1.4591; 32.5% $EtP(O)(OCH_2Ph)OCH:CCl_2$,
$b_{0.5}$ 132-33°, 1.2805, 1.5220; 82.8% $EtP(O)(OCH_2CH:CH_2)OCH:CCl_2$, $b_{0.5}$ 76-78°,
1.2623, 1.4740. Similar use of appropriate $EtP(OR)NR'_2$ similarly gave:
52% $EtP(O)(OCH:CCl_2)NMe_2$, b_2 80-82°, 1.2482, 1.4714; 50% $EtP(O)(OCH:CCl_2)-$
NEt_2, b_1 92-93°, 1.1974, 1.4758. Et_2POMe gave 70% $Et_2P(O)OCH:CCl_2$, $b_{0.5}$
81-83°, 1.2465, 1.4810. Preliminary tests showed that these products have
a high order of biological activity and are being tested further. The
intermediates used, prepd. by known methods, included new esters: $EtP-$
$(OCH_2Ph)_2$, $b_{1.5}$ 140-41°, 1.0761, 1.5499; $EtP(OCH_2CH:CH_2)_2$, b_{11} 65-67°,
0.9896, 1.4553; $EtP(OAm)_2$, b_2 81-82°, 0.8834, 1.4390; also listed are:
$EtPNMe_2Cl$, b_{16} 51-52°, 1.0271, 1.4855 and $EtPNMe_2(OCHMe_2)$, b_{27} 71-73°,
0.8932, 1.4377.

Organophosphorus

Synthesis of hetreo-organic compounds of general formula $Me_n(OSiR_3)_n$.
B. I. Yakovlev and N. V. Vinogradova. Zhur. Obshchei Khim. 29, 695-6 (1959).
Reaction of 6.5 g. $Ti(OEt)_4$ and 19.6 g. Et_3SiOH gave 9.3 g. $(Et_3SiO)_4Ti$,
$b_{3.5}$ 199-202°, $d_4^{20.5}$ 0.917, dielectric constant 2.18 at 20° at 1000 ops.
Reaction of 2 g. B_2O_3 and 25 g. Et_3SiOH gave 9.2 g. $B(OSiEt_3)_3$, b_3 152-4°,
d_{18} 0.8942, n_D^{21} 1.4375. Reaction of 34 g. Et_3SiOH with 4 g. Na, followed by
6.8 g. PCl_3 gave 9.3 g. $(Et_3SiO)_3P$, b_3 164-6°, d_{18} 0.9308, n_D^{21} 1.4518. The
use of $POCl_3$ similarly gave $(Et_3SiO)_3PO$, b_3 181-3°, $d_4^{20.5}$ 0.9658, n_D^{21} 1.4460.

by Organophosph...

Application of Hammett equation to the theory of tautomeric equilibrium.
Thiono-thiolo tautomerism of thiophosphoric compounds.

M.I.Kabachnik, T.A.Mastryukova, A.E.Shipov and T.A.Melent'eva (Inst. Het-
ero-Org. Compds., Moscow). Doklady Akad. Nauk SSSR, 124, 1061-64 (1959).
Cf. this J. 83, 407, 859 (1952); Uspekhi Khim. 25, 137 (1956); Zhur. Ob-
shchei Khim. 25, 684 (1955); this J. 104, 861 (1955); 110, 393 (1956);
83, 859 (1952).

The ionization constants of 2 tautomeric forms of a substance may be exp-
ressed through the Hammett equation form of $pK = pK^0 - \rho \Sigma \sigma$, for each form.
Since the actual exptl. detn. of pK ~~xxxxxxxxxxxxxxxxxxxxx~~ gives
only some effective constants K_a, rather than the constants of the indiv-
idual forms, it is possible to derive the formula $K_T = 10^a - 1$, where a
is the deviation (on ordinate axis) of the exptl. pK curve from the
asymptote which coincides with the straight line $pK_1 = pK_1^0 - \rho \Sigma \sigma$, and
$pK_a = pK_1 - \log(K_T + 1)$, where pK_a is the result of an exptl. detn. of
the ionization constant of a tautomer system and pK_1 is that of one of
the tautomeric forms and K_T is the tautomerism equil. constant. This
equation permits an exptl. soln. of tautomeric equil. problems, as follows.
The apparent ionization constants are detd. by some method for a series
of substances of one class, differing only by the nature of substituents,
and the data are used to construct a plot of pK vs. $\Sigma \sigma$. If the plot is
a straight line, the tautomeric equil. is shifted almost totally to one
tautomer. If the plot is a curve, part of which fits the rectilinear form
and the remainder curves away from the latter, this shows a displacement
of the equil. toward one of the forms, and the deviation a, cited above,
measured on the plot, affords a detn. of the tautomeric equil. constant K_T.
In the present paper this principle was applied to a series of P-S acid
derivs. with the indicated amount of the thiolo form (in %) being estd.:
$(PhO)_2PSOH$, m. 86-87°, 80% in 7% EtOH, 79% in 80% EtOH; $(MeO)_2PSOH$, (Na salt
with m. 156° was used), 74% in 7% EtOH, 68% in 80% EtOH; $(EtO)_2PSOH$, $b_{2.5}$

$106\text{-}107^\bullet$, n_D^{20} 1.4719, d_{20} 1.1806, 54% and 46%; (iso-PrO)$_2$PSOH, $b_{1.5}$ 89-90$^\bullet$, 1.4592, 1.0906, 54% and 29%; (p-ClC$_6$H$_4$O)$_2$PSOH, m.103-104$^\bullet$, 54% and 28%; (iso-BuO)$_2$PSOH, $b_{0.05}$ 83.5-4$^\bullet$, 1.4570, 1.0386, 52% and 27%; (PrO)$_2$PSOH, $b_{0.09}$ 108.5-9.5$^\bullet$, 1.4678, 1.1023, 50% and 24%; (BuO)$_2$PSOH, $b_{0.08}$ 88-9$^\bullet$, 1.4654, 1.0672, 38% and 11%; MeP(OEt)OSH, b_1 72.5°, 1.4927, 1.1800, 19% and 2%; PhP(OPh)OSH, m. 141-42°, 18% and 8%; MeP(OCH$_2$CHMe$_2$)OSH, $b_{0.5}$ 112-2.5$^\bullet$, 1.4819, 1.0824, 16% and 1%; MeP(OPr)OSH, $b_{2.5}$ 106-7$^\bullet$, 1.4883, 1.1293, 15% and 1%; EtP(OEt)OSH, b_2 84.5-5.5$^\bullet$, 1.4916, 1.1337, 14% and 1%; MeP(OBu)OSH, $b_{0.5}$ 90°, 1.4891, 1.0998, 12% and 0.8%; PrP(OEt)PSH, b_2 101-102$^\bullet$, 1.4875, 1.0974, 12% and 0.8%; BuP(OEt)OSH, $b_{0.015}$ 64.5-65°, 1.4831, 1.0721, 10% and 0.6%; EtP(OBu)OSH, b_1 110$^\bullet$, 1.4875, 1.0810, 9% and 0.4%; iso-BuP(OBu)OSH, $b_{0.1}$ 82$^\bullet$, 1.4821, 1.0321, 5% and 0.2%; Et$_2$PSOH, $b_{1.5}$ 88.5-89°, 1.5262, 1.10-90, 1% and 0.1%; Pr$_2$PSOH, b_2 98.5-99°, -.-, 1% and 0%; iso-Bu$_2$PSOH, $b_{0.25}$ 81-1.5°, -.-, 0.8% and 0%; iso-Pr$_2$PSOH, m. 69.5-70.5°, 0.5%, 0%; (MeEtCH)$_2$-PSOH, m. 102-102.5°, 0.4% and 0%; (Me$_3$C)$_2$PSOH, m. 144-45°, 0% and 0%. The pK detns. were made potentiometrically with partially neutralized solns. in the alc. concns. indicated above. The equil. constants found fit the Hammett equation satisfactorily. Thus the deviation of pK values from the rectilinear dependence of pK_a on σ may be used for estn. of the tautomeric equil. position.

a   *Organophosphorus*

A method of synthesis of acid esters of phosphinic acids.
M. I. Kabachnik, E. N. Tsvetkov and Chzhan Zhun Yui (Inst. Hetero-org.
Compds., Moscow). Doklady Akad. Nauk S.S.S.R. 125, 1260-2 (1959).
Cf. Arbuzov et al. Izvest. Akad. Nauk SS R, Otdel. Khim. Nauk 1952,956.
Also cf. Kabachnik et al. this j. 117, 817 (1957).
The previously described reaction of prepn. of ~~XXXXXXXXXXXXXXXXXXXX~~
$RP(OR)_2$ from $(RO)_2PCl$ and RMgX was extended to the conversion of the former
by direct hydrolysis to $ROP(O)RR$. Thus, addn. of 0.11 mole RMgX in Et_2O
dropwise to 0.1 mole $(RO)_2PCl$ in 50 ml. Et_2O and $-60°$, followed by warming
to $20°$, addn. of 50 ml. of 5% NH_4Cl soln., standing overnight, extn. of
the aq. layer with $CHCl_3$, drying the combined org. layers and distn.
(all operations done under N_2) gave the desired $RP(O)(OR')R$ (R and R'
shown, resp.): Me, Bu, 55.1%, b_2 47-8°, n_D^{20} 1.4321, d_{20} 0.9959; Et, Bu,
53%, b_{10} 94-5°, 1.4350, 0.9769; Pr, Bu, 60%, b_2 67-7.5°, 1.4347, 0.9635;
isoPr, Bu, 59.1%, $b_{2.5}$ 58.5-60.2°, 1.4321, 0.9581; Bu, Et, 54.6%, $b_{1.5}$
49-9.5°, 1.4350, 0.9834; iso-Bu, Et, 54%, b_6 76-7°, 1.4310, 0.9730; Ph, Bu,
58.1%, b_1 99.2-100°, 1.5144, 1.0758; $PhCH_2$, Bu, 58.4%, b_2 113-15.2°,
1.5160, 1.0646. $PhCH_2P(O)(OBu)H$ treated with Na in MePh gave the Na salt
which with $PhCH_2Cl$ after reflux of 3 hrs. gave $(PhCH_2)_2P(O)OBu$, 67%, m.
77.5-8° (from petr. ether), which boiled 10 hrs. with KOH soln. gave
$(PhCH_2)_2PO_2H$, m. 191.5-2.3°. Similarly $PrP(O)(OBu)H$ gave 58.7% $Pr_2P(O)OBu$,
$b_{2.5}$ 90.5-1.5°, 1.4419, 0.9389.

Organic insectefungicides. XLI. Reaction of dialkyl phosphochlorothioates and thiophosphoryl chloride with phenols in the presence of tertiary amines. Ya. A. Mandel'baum, N. N. Mel'nikov and Z. M. Bakanova (Fertil. and Insect-ofungic. Inst., Moscow). Zhur. Obshchei Khim. 29, 1149-51 (1959). cf. Uspekhi Khim. 22, 253 (1953).

To 0.1 mole ArOH and 0.105 mole Et_3N in PhBr, PhCl, Me_2CO or MeOH, EtOH or iso-PrOH (the latter is best for nitro derivs.) there was added at 10-14° 0.1 mole $(RO)_2PSCl$; after 3 hrs. the mixt. was treated with H_2O, and the product was washed with aq. Na_2CO_3 and distd. Thus were prepd.: 77.5% $(MeO)_2PSOC_6H_4NO_2$-p, b_2 158°, m. 36°; 80% $(MeO)(EtO)PSOC_6H_4NO_2$-p, $b_{0.15}$ 120-1°, d_{20} 1.3182, n_D^{20} 1.5470; 82% $(EtO)_2PSOC_6H_4NO_2$-p, $b_{0.04}$ 115°, 1.2455, 1.5385; 60% $(EtO)_2PSOPh$, $b_{0.1}$ 117-22°, 1.1763, 1.5110; 47% $(EtO)_2PSOC_6H_3Cl_2$-o,p, $b_{0.3}$ 150-4°, 1.3085, 1.5285. Addn. of 0.1 mole ArOH and 0.1 mole Et_3N in 40 ml. C_6H_6 at 10-20° to 0.2 mole $PSCl_3$ in 50 ml. C_6H_6, followed by filtration and washing with H_2O gave: 43% $PhOPSCl_2$, b_{15} 129°, 1.4050, 1.3730, and 53% p-$O_2NC_6H_4OPSCl_2$, $b_{0.15}$ 130-5°, m. 54°.

Organic insectofungicides. XXXVII. Synthesis of some mixed esters of thio- and dithiophospheric acids.

Ya. A. Mandel'baum, N. N. Mel'nikov and P. G. Zaks (Fertil. and Insecto- fungicide Res. Inst., Moscow). Zhur. Obshchei Khim. 29, 283-5 (1959). cf. Trudy N.I.U.I.F., p. 438 (1957).

Refluxing dry Na or K salts of $(EtO)_2POSH$ or $(EtO)_2PS_2H$ with amido or esters of $ClCH_2CO_2H$ in Me_2CO 5-6 hrs. gave after filtration: $(EtO)_2PSOCH_2COR$ (R shown): NMe_2, 64%, $b_{0.4}$ 135-7°, d_{20} 1.1832, n_D^{20} 1.4810; NEt_2, 70%, $b_{0.35}$ 147°, 1.1336, 1.4800; $NHC_6H_4NO_2$-o, 53%, $b_{0.3}$ 150-5°, 1.3233, 1.5570; $NH-C_6H_4NO_2$-m, 62%, m. 110°; (I) p-isomer, 75%, m. 111°; $OC_6H_4NO_2$-m, 52%, $b_{0.3}$ 130°, 1.2689, 1.5085; p-isomer, 48%, $b_{0.5}$ 160°, 1.2806, 1.5187; OC_6H_4Cl-p, 72%, $b_{0.2}$ 125-35°, 1.2787, 1.5210; $OC_6H_3Cl_2$-o,p, 45%, $b_{0.1}$ 174-7°, 1.3591, 1.5310; SEt, 70%, $b_{0.2}$ 133-6°, 1.2041, 1.5013; SPh, 66%, $b_{0.2}$ 173-5°, 1.2476, 1.5565; SC_6H_4Cl-p, 66%, $b_{0.2}$ 150-60°, 1.3141, 1.5670; ~~NHCHCOOCHCHCHCH etc.~~ ~~etc.~~;

The following were prepd. similarly: $(EtO)_2PS_2CH_2COR$: NMe_2, undistillable, 59%, 1.1985, 1.5210; NEt_2, undistillable, 47%, 1.1478, 1.5136; $NHC_6H_4NO_2$-o, undistillable, 83%, 1.3992, 1.5950; m-isomer, 93%, m. 102°; p-isomer, 84%, m.112°; $OC_6H_4NO_2$-m, 45%, m. 66-8°; p-isomer, undistillable, 48%, 1.3135, 1.5640; OC_6H_4Cl-p, 80%, $b_{0.15}$ 170°, 1.2820, 1.5540; SEt, $b_{0.1}$ 140-3°, 72%, 1.1961, 1.5370; SPh, undistillable, 97%, 1.2321, 1.5845; SC_6H_4Cl-p, 98%, undistillable, 1.3000, 1.5890. All were less active than Parathion in tests on grain weevil. I was the most active contact insecticide in the group.

Synthesis of (organophosphorus) compounds from hydrocarbons and their derivatives. IX. Oxidative chlorophosphonation of 1-butene, 2-butene and cyclohexene. Yu. M. Zinov'ev and L. Z. Soborovskii. Zhur. Obshchei Khim. 29, 615-9(1959). Passage of O_2 and 1-butene into PCl_3 gave a range of products $RClPOCl_2$, which on fractionation gave (percentages refer to phosphonic dichloride obtained): 26.8% mixed $EtCHClCH_2POCl_2$ and $EtCH(CH_2Cl)POCl_2$, b_2 85-6°, d_{20} 1.3925, n_D^{20} 1.4925, and 73.2% $MeCHClCHMePOCl_2$, b_2 73-4°, 1.3950, 1.4857. 2-Butene gave 100% $MeCHClCHMePOCl_2$, b_2 70-4°, 1.3831, 1.4820. BuCl gave 9.5% $PrCHClPOCl_2$, b_2 78-9°, 1.3779, 1.4886, 20.5% $EtCH(CH_2Cl)POCl_2$, b_2 84-5°, 1.3948, 1.4946, 54% $MeCH(POCl_2)CH_2CH_2Cl$, b_2 95-8°, 1.4028, 1.4963, and 16% $ClCH_2(CH_2)_3POCl_2$, b_2 110-3°, 1.3952, 1.4950. 2-Chlorobutane gave mixed isomers $C_4H_8ClPOCl_2$, $b_{2.5}$ 85-93°, 1.3903, 1.4905. Contrary to Isbell et al. (JACS 78, 6042(1956)), passage of O_2 into 41 g. cyclohexene and 455 g. PCl_3 at 20° gave 40.4% crude product, b_5 120-35°. Fractionation of this gave a high boiling fraction of

Organic insectofungicides. XXXVIII. Reaction of thiophosphoryl chloride and alkyl dichlorophosphorethioates with alcohols.

N. N. Mel'nikov, Ya. A. Mandel'baum and P. G. Zaks (Fertilizer and Insecto-fungicide Res. Inst., Moscow). Zhur. Obshchei Khim. 29, 522-6 (1959). Cf. this J. 27, 1908 (1957).

To 1 mole $PSCl_3$ there was added with stirring and cooling to 15-20° 10 moles MeOH and after stirring 3 hrs., the mixt. was washed with H_2O and the residue yielded 53% $(MeO)_2PSCl$, b_{16} 65-6°, d_0^{20} 1.3351, n_D^{25} 1.4834; similarly 60 moles EtOH in 24 hrs. gave 34% $(EtO)_2PSCl$; 60 moles PrOH gave in 27 hrs. 46% $(PrO)_2PSCl$, and 60 moles BuOH gave in 29 hrs. 48% $(BuO)_2PSCl$. The excess ROH was either washed out with H_2O or distd. in vacuo. Similar reaction but requiring longer stirring was used to prepare $(RO)_3PS$, but only the reaction with MeOH gave the desired results. Thus, 60 moles MeOH and 1 mole $PSCl_3$ in 48 hrs. at 20° gave 6% $(MeO)_3PS$, b_{13} 72-4°, 1.2192, 1.4599. Similarly 10 moles of MeOH and 1 mole $MeOPSCl_2$ in 6 hrs. at 5-10° gave 71% $(MeO)_2PSCl$, b_{10} 56-7°, d_0^{20} 1.3351, n_D^{20} 1.4834; 40 moles EtOH and 1 mole $EtOPSCl_2$ gave in 24 hrs. at 20-30° 61% $(EtO)_2PSCl$; similarly was prepd. 63% $(PrO)_2PSCl$, b_{17} 109-11°, 1.1648, 1.4650, and 60% $(BuO)_2PSCl$, b_{15} 140-2°, 1.0695, 1.4601. Reaction of various $ROPSCl_2$ with MeOH (10-15 moles) gave in 1.5-4 hrs. at 20-30° the following mixed products: 81% $(MeO)(EtO)PSCl$, b_{17} 80-1°, d_{20} 1.2506, 1.4740; 65% $(MeO)(PrO)PSCl$, b_{25} 107-10°, 1.1852, 1.4650; 77% $(MeO)(BuO)PSCl$, $b_{0.3}$ 45-7°, 1.1830, 1.4765; 90% $(MeO)(iso-BuO)PSCl$, b_{22} 110-4°, 1.1364, 1.4600; 92% $(MeO)(iso-AmO)PSCl$, b_{32} 138-40°, 1.1361, 1.4672. Similarly 40 moles MeOH and 1 mole $MeOPSCl_2$ in 26 hrs. at 20° gave 32% $(MeO)_3PS$, while 20 moles MeOH and 1 mole $(MeO)_2PSCl$ in 24 hrs. at 20° gave a 56% yield of $(MeO)_3PS$. Similarly 20 moles ROH and $(MeO)_2PSCl$ in 24 hrs. at 20-30° gave: 46% $(MeO)_2PS(OEt)$, b_{25} 96°, d_{20} 1.1507, n_D^{20} 1.4520; 73% $(MeO)_2PS(OPr)$, b_{22} 104-5°, 1.1203, 1.4571; and 30% $(MeO)_2PS(OBu)$, b_{20} 114°, 1.0941, 1.4560. Thus, $PSCl_3$ and $ROPSCl_2$ react like other polyfunctional acid chlorides and their reaction with ROH is not limited to but one substitution stage.

a Organophos—

Difluorochloromethane as a difluoromethylating agent. II. Reaction of difluorochloromethane with dialkyl sodiophosphites.

L. Z. Soborovskii and N. F. Baina. Zhur. Obshchei Khim. 29, 1144-6 (1959). Passage of 52 g. $CHClF_2$ at 30-5° into a soln. of 11.5 g. Na and 69 g. $(EtO)_2PHO$ in petr. ether gave a ppt. of NaCl and on the following day the filtered soln. gave 48.6% $CHF_2PO(OEt)_2$, b_{12} 85.6-6.5°, d_{20} 1.1934. Similarly were prepd: 48.5% di-iso-Pr ester, b_{12} 89-90°, d_{20} 1.1135, n_D^{20} 1.3670; 67.3% di-Bu ester, b_{12} 124-5°, 1.0915, 1.4084 (in this case the pptn. of NaCl occurred only after the addn. of a little H_2O). The latter (15 g.) was treated gradually with 25 g. PCl_5 at 70°, yielding 11.5 g. mixed BuCl and PCl_3, $POCl_3$ and 3 g. CHF_2POCl_2, b_{50} 50-2°; some 50% of the mixt. was an undistillable mass. If this reaction is run with equimolar proportion of PCl_5 the C-P bond is ruptured and the main product is $BuOPOCl_2$, b_{17} 80°. Reaction of PCl_5 with $CHF_2PO(OEt)_2$ similarly gave $EtOPOCl_2$ and only a trace of CHF_2POCl_2. Reaction of $CHClF_2$ with $(MeO)_2PONa$ gave only a trace of $CHF_2PO(OMe)_2$ and much $(MeO)_2PHO$ if the reaction is run in ROH; this reaction course is ascribed to facile formation of $MeOCHF_2$ and the removal of MeONa component of the equil. mixt. of MeONa-$(MeO)_2PHO$.

4

$C_6H_{10}ClPOCl_2$, b_3 127-30°, 1.4162, 1.5287, and a low boiling fraction (crude) b_4 118-24°, which distd. from activated C to eliminate residual HCl, gave $C_6H_9POCl_2$, b_2 99-102°, 1.3520, 1.5250.

Synthesis of (organophosphorus) compounds from hydrocarbons and their derivatives. X. Oxidative chlorophosphonation of some ethylene derivatives. L. Z. Soborovskii, Yu. M. Zinov'ev and T. G. Spiridonova. Zhur. Obshchei Khim. 29, 1139-41 (1959). cf. Doklady Akad.Nauk SSSR 109, 98(1956) and this j. 28, 1870(1958).

Passage of O_2 at $0°$ into 20 g. ($:CHCl)_2$ and 400 g. PCl_3 gave 18.8 g. (40%) $Cl_2CHCHClPOCl_2$, b_3 89-92°, d_{20} 1.7172, n_D^{20} 1.4990, which is slowly attacked by H_2O. Passage of O_2 into 34 g. $CH_2:CHBr$ and 400 g. PCl_3 gave 24.2 g.(39%) material, $b_{0.05}$ 93-125°, which on further fractionation gave 8 g. $BrCH:CH-POCl_2$, b_3 81-2°, 1.7415, 1.4889, and 3.7 g. $BrCH_2CHClPOCl_2$, b_3 99-100°, 1.9720, 1.5378. Passage of 15 l. dry $CH_2:CHF$ at -70° into 275 g. PCl_3 and percolation of O_2 at -70° until the mass crystallized gave 6.3% (7.6 g.) $C_2H_3FClPOCl_2$, b_{30} 109°, 1.6531, 1.4715. Passage of O_2 into 16 g. $CHF:CHCl$ and 300 g. PCl_3 at -5° gave 11.7 g. (25.2%) $C_2H_2FCl_2POCl_2$, b_3 66-70°, 1.6893, 1.4640. Passage of O_2 at 20-5° into 60 g. $CH_2:CHSO_2F$ and 400 g.PCl_3 gave 13.5 g. (9.3%) $FSO_2C_2H_3ClPOCl_2$, b_3 95-7°, 1.7264, 1.4618. Similar reactions attempted with vinylidene chloride, trichloroethylene and tetrachloroethylene either gave a polymer or failed to proceed (last 2). Passage of Cl_2 at 0-5° into $CH_2:CHBr$ in CCl_4 gave 52% $BrClCHCH_2Cl$, b_{750} 134-5°, 1.6663, 1.5136.

/ **Vinyl esters of phosphorous acid.** d *Organic phosphorus*

A.N.Nesmeyanov, I.F.Lutsenko, Z.S.Kraits and A.P.Bokovoi (M.V.Lomonosov State Univ.,Moscow). Deklady Akad.Nauk SSSR, 124, 1251-54 (1959). Cf. Nesmeyanov et al. Izvest.Akad.Nauk SSSR, otdel.khim.nauk 1949,601. To 0.1 mole $Hg(CH_2CHO)_2$ and 0.1 mole Et_3N in 250 ml. isopentane was added over 1 hr. with vigorous stirring 0.1 mole $(EtO)_2PCl$ in 50 ml. isopentane, after which 0.1 mole $Hg(CH_2CHO)_2$ and 0.1 mole Et_3N was added, followed by 0.1 mole $(EtO)_2PCl$ and the whole was then stirred 1 hr. longer. The liquid portion was sepd. and distd. yielding 65% $(EtO)_2POCH:CH_2$, b_{28} 58-59°, n_D^{20} 1.4258, d_{20} 0.9787. While the same product also forms from $ClHgCH_2CHO$, the yields are very low and the product difficult to purify. The following were prepd. similarly, except that the Me ester required the use of $PhNEt_2$ in place of Et_3N. $(MeO)_2POCH:CH_2$, 46%, b_{80} 55-56°, 1.4255, 1.0406; $(PrO)_2PO$-$CH:CH_2$, 62%, b_3 53-54°, 1.4322, 0.9518; $(BuO)_2POCH:CH_2$, 70%, b_4 85-86°, 1.4360, 0.9381; $(PhO)_2POCH:CH_2$, 56%, b_3 143-44°, 1.5575, 1.1567. To 250 ml. isopentane there was added over 5 hrs. in 4 equal portions 133 g. $Hg(CH_2$-$CHO)_2$, 45.5 g. Et_3N and 20.5 g. PCl_3; after stirring 1 hr. there was formed 46% $P(OCH:CH_2)_3$, b_{50} 51-52°, 1.4485, 1.0262. To 0.1 mole $Hg(CH_2CHO)_2$ and 0.1 mole Et_3N in 250 ml. isopentane there was added over 1 hr. 0.05 mole $EtOPCl_2$ in 25 ml. isopentane; over 4 hrs. there was thenadded 120 g. Hg-$(CH_2CHO)_2$, 40.4 g. Et_3N and 29.4 g. $EtOPCl_2$ after which the mixt. was stirred 1 hr. and yielded after usual treatment 60% $EtOP(OCH:CH_2)_2$, b_{30} 57-58°, 1.4380, 1.0015; similarly were prepd.: 60% $MeOP(OCH:CH_2)_2$, b_{60} 60-61°, 1.4390, 1.0368; 60% $PrOP(OCH:CH_2)_2$, b_{11} 56-57°, 1.4392, 0.9908; 55% $BuOP$-$(OCH:CH_2)_2$, b_7 63°, 1.4412, 0.9873; 79% $PhOP(OCH:CH_2)_2$, b_{10} 108-109°, 1.5151, 1.1037. The divinyl esters tended to polymerize during distn. and only by addn. of an equivalent amount of the base was it possible to

3

suppress this tendency. The vinyl esters are readily hydrolyzed with H_2O with evolution of heat. Addn. of SO_2-fuchsine, immediately gave the characteristic color test. The trivinyl ester is hydrolyzed rapidly by even just traces of moisture, forming a gelatinous mass which heats up rapidly and darkens, evolving AcH. Heating the vinyl esters with S on a steam bath several hrs (6-8) gave the following thiophosphates: $(EtO)_2P(S)OCH:CH_2$, 70%, $b_{7.5}$ 82°, 1.4562, 1.0904; $(PrO)_2P(S)OCH:CH_2$, 64%, b_6 97°, 1.4581, 1.0505; $(BuO)_2P(S)OCH:CH_2$, 68%, b_8 126-27°, 1.4575, 1.0195; $(PhO)_2P(S)OCH:CH_2$, 50%, b_2 163-64°, 1.5655, 1.2164; $EtOP(S)(OCH:CH_2)_2$, 62%, b_7 72-73°, 1.4654, 1.1017; $BuOP(S)(OCH:CH_2)_2$, 65%, b_9 96°, 1.4654, 1.0617; 74% $PhOP(S)(OCH:CH_2)_2$ b_{10} 134-35°, 1.5268, 1.1719. Attempted oxidation by various means of the vinyl phosphites failed to yield the desired vinyl phosphates since polymerization intervened. Preliminary expts. indicate that the Arbuzov isomerization of the vinyl esters is more difficult than in the satd. esters. The addn. of S to Ph and Ph_2 esters requires heating to 130-50°.

b Organophosphorus

Phosphorylated chlorovinyl ketones. Preparation of phosphorylated chloro-
vinyl ketones from vinyl acetate and isopropenyl acetate.

I. F. Lutsenko and M. Kirilov (M. V. Lomonosov State Univ., Moscow). Doklady
Akad. Nauk S.S.S.R. 128, 89-91(1959).

To 125 g. PCl_5 suspended in CCl_4 was added over 45 min. 29.5 g. CH_2:CHOAc
at 15-17° and after 2 hrs. with gradual heating to 40°, the mixt. was
treated with SO_2 with cooling, and distd. yielding 85% $Cl_2CHCHAcPOCl_2$,
b_2 94-5°, n_D^{20} 1.5100, d_{20} 1.5464. This (51.6 g.) in 150 ml. Et_2O was
treated over 0.5 hr. with 18.4 g. abs. EtOH in 25 ml. Et_2O and after 2 hrs.
at 25-30°, the mixt. was air blown 1 hr. and distd. yielding 62.5%
$CHCl_2CHAcPO(OEt)_2$, b_2 111-12°, 1.4620, 1.2465. If this esterification is
run in the presence of pyridine, there is formed a 52% yield of the ester
contg. some of the $CTCl$:CAcPO(OEt)$_2$ (I) even after several redistns. Heating
the ester with Et_3N in C_6H_6 2 hrs. gave 88% I, b_2 102-3°, 1.4645, 1.1861.
Similarly 83.2 g. PCl_5 and 20 g. CH_2:CMeOAc gave 70% MeCCl:CAcPOCl$_2$, $b_{1.5}$
112-13°, 1.5233, 1.4413; the $MeCCl_2CHAcPOCl_2$ was unstable and lost HCl
directly. Reaction of the chloride with EtOH in the presence of pyridine
gave 75% MeCCl:CAcPO(OEt)$_2$, b_1 114-5°, 1.4710, 1.1726.

Ethylenimine derivatives. I. Ethylenimides of phosphoric acid.
A. A. Krepacheva and V. A. Parshina (S. Ordzhonikidze All Union Chem. Pharm.
Res. Inst., Moscow). Zhur. Obshchei Khim. 29, 556-60 (1959). Cf. Bestian,
Ann. 566, 210 (1950); US Pat 2,606,900(C.A. 47, 5423 (1953); US Pat. 2,654,-
758 (C.A. 48, 10053(1954); US Pat. 2,670,347 (C.A. 49, 2481(1955).

To 14.3 g. $POCl_3$ in abs. Et_2O was added at 0° 25 g. $2-C_{10}H_7NH_2$ in Et_2O and
after 1 hr. with cooling and 3 hrs. at room temp., there formed after filtr-
ation and evapn. 52.8% $2-C_{10}H_7NHPOCl_2$, m. $115-17^\circ$ (from $C_6H_6-Et_2O$); thus
were prepd. also: $PhNHPOCl_2$, 42.7%, m. 70°; $p-ClC_6H_4NHPOCl_2$, 74%, m. 103-4;
$p-IC_6H_4NHPOCl_2$, 48%, m. $105-7^\circ$; $m-O_2NC_6H_4NHPOCl_2$, 66.8%, m. $85-6^\circ$; $p-MeOC_6H_4-$
$NHPOCl_2$, 41.3%, m. $71-2^\circ$; $p-EtO_2CC_6H_4NHPOCl_2$, 68.8%, m. $100-2^\circ$; $m-ClC(O)C_6H_4-$
$NHPOCl_2$, 43%, m. $110.5-11.5^\circ$; $2,4-(Cl_2PONH)_2MeC_6H_3$, 53.5%, m. $153-4^\circ$. The
above products were best prepd. by refluxing $POCl_3$ with HCl salt of the amine.
Addn. at 6° of 8.39 g. $PhNHPOCl_2$ in C_6H_6 to 3.44 g. ethylenimine and 8.08 g.
Et_3N in C_6H_6, stirring 4 hrs. at room temp. and setting the mixt. aside until
the next day gave after filtration and evapn. 5% $PhNHPO(NCH_2CH_2)_2$, m. $143-4^\circ$.
Similarly were prepd.: 27% $p-ClC_6H_4NH$ analog, m. $170-1.5^\circ$; 77% $p-IC_6H_4NH$ ana-
log, m. $176-7^\circ$; 57% $m-O_2NC_6H_4NH$ analog, m. $166-7^\circ$; 54.5% $p-MeOC_6H_4NH$ analog,
m. $102-3^\circ$; 71.7% $p-EtO_2CC6H_4NH$ analog, m. $151-2^\circ$; $m-(CH_2CH_2NCO)C_6H_4NH$ analog

3

82%, m. 131-2.5°; 38% 2-$C_{10}H_7$NH analog, m. 148°; 55.9% 2,4-$(CH_2CH_2NPONH)_2$Me-C_6H_3, m. 205-6°. To 1.72 g. ethylenimine, 4.04 g. Et_3N and 20 ml. C_6H_6 was added at 6° 4.22 g. $PhOPOCl_2$ in 15 ml. C_6H_6; after 4-5 hrs. stirring and allowing to warm up overnight, the filtered and evapd. soln. gave 80% $PhOP(O)(NCH_2CH_2)_2$, m. 58-9°; similarly was prepd. 64% $p-O_2NC_6H_4O$ analog, m. 73.5-74°. The deriv. based on m-aminobenzoic acid was verified as to the above structure as an ethylenimide by means of infrared spectrum, which showed the 1673 cm^{-1} band typical of carbonamide structures.

Organophosphorus

Chlorides of esters of phosphonocarboxylic acids. I. Synthesis of P-mono-
chlorides of dialkyl esters of phosphonocarboxylic acids.

K. A. Petrov, F. L. Maklyaev and M. A. Korshunov (Milit. Acad. Chem. Def-
ence). Zhur. Obshchei Khim. 29, 301-5 (1959).

Gradual addn. of 0.21 mole powd. PCl_5 to 0.2 mole $(RO)_2P(O)(CH_2)_xCO_2R$, and
stirring 15-30 min. at 18° and 20-40 min. at 30-50°, followed by decompn.
of unreacted PCl_5 with SO_2 at 18° gave the following products when the
reaction is run in 1 vol. dry CCl_4: 63% $(MeO)ClP(O)CO_2Me$, b_1 85-6°, d_{20}
1.4167, n_D^{20} 1.4475; 82% $(EtO)ClP(O)CO_2Et$, b_5 107-8°, 1.2410, 1.4385; 81%
$(BuO)ClP(O)CO_2Et$, $b_{0.35}$ 98-101°, 1.1977, 1.4387; 56% $(BuO)ClP(O)CO_2Bu$, b_{3-4}
133-4°, 1.1326, 1.4455; 84% $(EtO)ClP(O)CH_2CO_2Et$, b_3 110-11°, 1.2584, 1.4476;
58% $(iso-PrO)ClP(O)CH_2CO_2Et$, $b_{0.25}$ 92-3°, 1.1947, 1.4430; 63% $(iso-AmO)ClP(O)$-
CH_2CO_2Et, $b_{0.03}$ 110-12°, 1.1384, 1.4463; 68% $(BuO)ClP(O)CH_2CO_2Et$, $b_{0.35}$ 120-
22°, 1.1551, 1.4440; 80% $(MeO)ClP(O)CH_2CH_2CO_2Me$, $b_{0.2}$ 92-4°, 1.3306, 1.4506;
81% $(EtO)ClP(O)CH_2CH_2CO_2Et$, $b_{0.1}$ 101-2°, 1.2502, 1.4555; 80% $(iso-Pr)ClP(O)$-
$CH_2CH_2CO_2Et$, $b_{0.05}$ 113-16°, 1.2352, 1.4486; 74% $(BuO)ClP(O)CH_2CH_2CO_2Et$, $b_{0.0}$
128-33°, 1.1526, 1.4520; 78% $(EtO)ClP(S)CH_2CH_2CO_2Et$, b_1 118-9°, 1.2207, 1.-
4621. Treatment of the appropriate chloride (2 g.) in C_6H_6 with cooling
with 88 ml. soln. of NH_3 in C_6H_6 and keeping the mixt. 24 hrs. in closed
flask gave after filtration and evapn. 0.78 g. $(EtO)H_2NP(O)CO_2Et$, m. 137°
(from $EtOH-C_6H_6$). Similarly was prepd. $H_2N(EtO)P(O)CH_2CO_2Et$, m. 103°
(from C_6H_6-petr. ether). Passage of Cl_2 at 5° into 31 g. $(MeO)_2P(O)CO_2Me$
in 100 ml. CCl_4
in 25.4 g. PCl_3 with ice/salt cooling 30 min., followed by heating to 40°
(PCl_5 ppt. dissolved) and the chlorination was repeated until all P^{III} had
reacted (3 hrs.); distn. gave $(MeO)ClP(O)CO_2Me$, identical with the above
in 63% yield. Similar chlorination of 32.1 g. $(EtO)_2P(O)CH_2CO_2Et$ and 21 g.
PCl_3 gave 70% corresponding monochloride, which decomposes at above 180°,
as doesthe phosphonoformic deriv. above Similarly was prepd. 56.6% (BuO)-
$Cl(O)PCH_2Bu$, which decomps. above 190°. Heating 5 g. $(EtO)_2P(O)CH_2CO_2Et$ and
7.95 g. $SOCl_2$ 9 hrs. at 80-90° gave 33% corresponding monochloride; similarl
was prepd. 42% $(MeO)ClP(O)CH_2CH_2CO_2Me$. $(EtO)ClP(S)(CH_2)_xCO_2Et$, b_2 123-5°.

Chlorides of esters of phosphonocarboxylic acids. II. Dichlorides of C-alkyl esters of phosphonocarboxylic acids.

K. A. Petrov, F. L. Maklyaev and M. A. Korshunov. Zhur. Obshchei Khim. 29, 585-8 (1959); cf. 29, 301 (1959).

$(RO)_2P(O)(CH_2)_nCO_2R$ react with excess PCl_5 to yield the corresponding P,P-dichlorides, with the carbalkoxy group not being affected even with large amt. of PCl_5 at $120°$. To 30 g. $(EtO)_2POCH_2CO_2Et$ was added over 1 hr. 39 g. PCl_5, the mixt. was heated 1.5 hrs. on a steam bath, then placed in a sealed tube and heated 5 hrs. at $115-20°$, after which SO_2 was introduced for 20 min. at room temp. and the residue was distd. yielding 68% $Cl_2P(O)CH_2CO_2Et$, $b_{0.05}$ $76-8°$, d_4^{23} 1.5038, n_D^{23} 1.4774; it decomposes above $135°$ to a brown tar. The above product does not form if the ester in PCl_3 soln. is treated with Cl_2; in this case chlorination of the CH_2 group occurs; thus passage of Cl_2 at below $60°$ (ice water cooling) through 100 g. above ester in 184 g. PCl_3 over 9 hrs., chilling to sep. PCl_5 passage of SO_2 and distn. gave a low b. product and 57.6% $Cl_2P(O)CCl_2CO_2Et$, b_8 $120-2°$, d_{20} 1.5603, n_D^{20} 1.4920. Heating 43 g. $(EtO)_2P(O)(CH_2)_2CO_2Et$ and 79.5 g. PCl_5 0.5 hr. at $65°$ and 1 hr. in sealed tube at $120°$ gave, after SO_2 treatment as above, 85.5% $Cl_2P(O)(CH_2)_2CO_2Et$, $b_{0.03-0.05}$ $89-91°$, d_{20} 1.5602, n_D^{20} 1.4640.. To 7.1 g. dry HF there was added with icecooling 11.7 g. I; after 50 min. at room temp. and 50 min. at $50°$, the residue was treated with 20 ml. dry Et_2O and 10 g. KF, after which the mass was filtered and distd. yielding $CHCl_2CO_2Et$ and evidently POF_3. Addn. of 5 g. I to 4 g. powd. KHF_2 resulted in heat evolution and after 1.5 hrs. at $100°$ and 2 hrs. at $140°$ there was isolated some $CHCl_2CO_2Et$ and low b. material.

Oxygen-Phosphorus

Synthesis of acid esters of dialkylaminoalkylphosphonic acids.

K. A. Petrov, F. L. Maklyaev and N. K. Blisnyuk. Zhur. Obshchei Khim. 29, 588-91 (1959).

Thermal decompn. of HCl salts of esters of dialkylaminoalkylphosphonates yields inner salts of esters, with elimination of an alkyl chloride; the final products are formulated as $R_2\overset{+}{N}HCH_2P(O)(OR)O^-$. Passage of dry HCl into 20.1 g. $Me_2NCH_2P(O)(OEt)_2$ (A) in 100 ml. dry Et_2O at $-15°$ gave 97.4% crystalline HCl salt, m. $95°$; this (11.8 g.), in Et_2O was slowly treated with 7.5 g. Et_3N and after 1 hr. at 35-40°, the ppt. amine salt was sepd. and the filtrate yielded 4.1 g. original free ester, b_1 95°. Similarly was prepd. syrupy $Et_2NCH_2P(O)(OBu)_2$.HCl (I); viscous glassy $Me_2NCH_2P(O)(OEt)_2$.HF (this heated to 130° failed to undergo any change). Heating 32 g. $Et_2NCH_2P(O)(OEt)_2$.HCl 20 hrs. on a steam bath gave 98% EtCl and a crystalline residue of 77.8% $Et_2NCH_2P(O)(OEt)OH$, m. 153° (from dry Me_2CO). Similarly I in 28 hrs. on a steam bath and 22 hrs. at 130-40° gave 97% BuCl and a syrupy $Et_2NCH_2P(O)(OBu)OH$ (sol. in H_2O, forming a neutral soln.). Heating I 20 hrs. on a steam bath gave 97% EtCl and 97% $Me_2NCH_2P(O)(OEt)OH$, m. 116° (from Me_2CO).

Organophosphorus

Synthesis of aminodiphosphonates and aminotriphosphonates.

K. A. Petrov, F. L. Maklyaev and N. K. Blisnyuk. Zhur. Obshchei Khim. 29, 591-4 (1959).

To 40 g. $(EtO)_2PHO$ and 4.5 g. $MeNH_2$ cooled to $-15°$ was added dropwise 22 g. 40% Formalin (temp. kept below 20°), the mixt. heated over 0.5 hr. to 100° and kept 15 min. at this temp.; after cooling, 5-10% NaOH was added, the mixt. extd. with C_6H_6, the org. layer washed with H_2O and distd. yielding 60% $MeN(CH_2P(O)(OEt)_2)_2$, $b_{0.5}$ 149-50°, d_{20} 1.1340, n_D^{20} 1.4470; similarly were prepd.: 54% $MeN(CH_2P(O)(OCHMe_2)_2)_2$, $b_{0.3}$ 146°, 1.0553, 1.4376; and 74.6% $MeN(CH_2P(O)(OBu)_2)_2$, b_1 195-7°, 1.0320, 1.4480. To 60 g. $(EtO)_2PHO$ and 19.9 g. 18.6% NH_4OH was added at $-10°$ 32.6 g. 40% Formalin; treatment as above gave 15.5% $NH(CH_2P(O)(OEt)_2)_2$, $b_{0.3}$ 150-1°, 1.1429, 1.4470 and 19.1%

(I)   2

$N(CH_2P(O)(OEt)_2)_3$, $b_{0.8}$ 202-4°, 1.1759, 1.4534. Excess phosphite and aldehyde tend to improve the yield of the latter product. Similarly, 50 g. $(BuO)_2$-PHO and 14.1 g. 18.6% NH_4OH with 23.2 g. 40% Formalin gave 21.7% $HN(CH_2-P(O)(OBu)_2)_2$, $b_{0.6}$ 195-6°, 1.0359, 1.4490 and same $N(CH_2P(O)(OBu)_2)_3$, $b_{0.8}$ 240-5°. Heating 6 g. $HN(CH_2P(O)(OEt)_2)_2$ and 20 ml. 1:1 HCl in sealed tube 5 hrs. at 140° gave after evapn. a glassy $HN(CH_2PO_3H_2)_2$, which titrates with NaOH as a tribasic acid; tetra-Ag salt, colorless crystals, darkens on heating. Similarly I gave pentabasic $N(CH_2PO_3H_2)_3$, a glassy solid; hexa-Ag salt, a colorless solid, darkening in light; decomps. on heating. Evidently the free acids exist in the form of zwitterions.

a Org. Phosphorus

C-Aryloxy-P,P-dimethoxyisophosphazeacyls and mixed triaryloxyisophosphazeacyl

A. V. Kirsanov and G. I. Derkach (Inst. Org. Chem., Acad. Sci., Kiev). Zhur. Obshchei Khim. 29, 600-5 (1959). Cf. this j.29, 241(1959). To 0.01 mole RCCl:NPO(OMe)$_2$ in 20 ml. C_6H_6 was added 0.0105 mole dry ArONa (exothermic) and after stirring until the mixt. became neutral (10-15 min., except for p-nitro deriv. which required 1-2 hrs. refluxing), NaCl was removed with H_2O, and the org. layer after evapn. gave RC(OR'):NPO(OMe)$_2$: R and R' shown resp.: Ph, p-ClC$_6$H$_4$, 63.6%, m. 85-7°; Ph, p-O$_2$NC$_6$H$_4$, 30%, m. 131-3°; p-ClC$_6$H$_4$, p-ClC$_6$H$_4$, 30.6%, m. 112-4°; p-ClC$_6$H$_4$, p-O$_2$NC$_6$H$_4$, 31.1%, m. 131-3°; p-O$_2$NC$_6$H$_4$, p-ClC$_6$H$_4$, 30%, m. 140-2°; p-O$_2$NC$_6$H$_4$, p-O$_2$NC$_6$H$_4$, 33.9%, m. 128-30°; m-O$_2$NC$_6$H$_4$, p-ClC$_6$H$_4$, 70%, m. 145-7°; m-O$_2$NC$_6$H$_4$, p-O$_2$NC$_6$H$_4$, 54.4%,m. 126-8°; 3,5-(O$_2$N)$_2$C$_6$H$_3$, p-ClC$_6$H$_4$, 44.4%, m. 100-3°; 3,5-(O$_2$N)$_2$C$_6$H$_3$, p-O$_2$N- C$_6$H$_4$, 73.4%, m. 151-3°. Similarly were prepd. RC(OR'):NPO(OPh)$_2$: 80% Ph, p- ClC$_6$H$_4$, m. 124-6°; 95.4% Ph, p-O$_2$NC$_6$H$_4$, m. 157-9°; p-ClC$_6$H$_4$, p-ClC$_6$H$_4$, 100%, m. 143-5°; 81%, p-ClC$_6$H$_4$, p-O$_2$NC$_6$H$_4$, m. 155-7°; p-O$_2$NC$_6$H$_4$, p-ClC$_6$H$_4$, 68.8%, m. 118-20°; 55.6% p-O$_2$NC$_6$H$_4$, p-O$_2$NC$_6$H$_4$, m. 162-4°; m-O$_2$NC$_6$H$_4$, p-ClC$_6$H$_4$, 60.9%, m. 124-6°; 99.9% m-O$_2$NC$_6$H$_4$, p-O$_2$NC$_6$H$_4$, m. 128-30°; 79.6% 3,4-(O$_2$N)$_2$C$_6$H$_3$, p-

3

ClC_6H_4, m. 181-3°; 68.9% 3,5-$(O_2N)_2C_6H_3$, p-$O_2NC_6H_4$, m. 204-6°. Refluxing $RCCl:NPO(OC_6H_4Cl-p)_2$ with dry p-$O_2NC_6H_4ONa$ in C_6H_6 gave $RC(OC_6H_4NO_2-p):NPO(OC_6H_4Cl-p)_2$ (R shown): Ph, 85.4%, m. 142-4°; p-ClC_6H_4, 79.2%, m. 151-3°; p-$O_2NC_6H_4$, 88.4%, m. 162-4°; m-$O_2NC_6H_4$, 85%, m. 133-5°; 3,5-$(O_2N)_2C_6H_3$, 77.6%, m. 209-10°. Similarly were prepd. $RC(OC_6H_4Cl-p):NPO(OC_6H_4NO_2-p)_2$: Ph, 69.3%, m. 180-2°; p-ClC_6H_4, 73.6%, m. 139-41°; p-$O_2NC_6H_4$, 66.9%, m. 217-9°; m-$O_2NC_6H_4$, 50.2%, m. 149-51°; 3,5-$(O_2N)_2C_6H_3$, 76.6%, m. 200-2°. The previously described method (cf. above ref.) gave: m-$O_2NC_6H_4CCl:NPO(OC_6H_4Cl-p)_2$, 80.1%, m. 120-3°; m-$O_2NC_6H_4CCl:NPO(OC_6H_4NO_2-p)_2$, 90%, m. 130-1°; 79.1% 3,5-$(O_2N)_2C_6H_4CCl:NPO(OC_6H_4Cl-p)_2$, m. 128-30°; 90% 3,5-$(O_2N)_2C_6H_3CCl:NPO(o-C_6H_4NO_2-p)_2$, m. 55-7°. Heating $RC(OC_6H_4NO_2-p):NPO(OPh)_2$ with 0.2 N aq. NaOH 1 hr. gave clear solns., which after concn. in vacuo and acidification to Congo red gave 60-70% known $RCONHPO(OR)_2$. Of the products reported here only $PhC(OC_6H_4NO_2-p):NPO(OMe)_2$ showed active contact insecticidal properties.

C-Chloro-P,P-dimethoxy- and C-chloro-P,P-diaryloxyisophosphazoacyls.
G. I. Derkach (Inst. Org. Chem., Acad. Sci., Kiev). Zhur. Obshchei Khim.
29, 241-5 (1959). Cf. Kirsanov et al. this J. 27, 1080 (1957).
Mixing 0.01 mole $(MeO)_2P(O)NHCOR$ with 0.01 mole PCl_5 in 10-15 ml. dry C_6H_6
or PhCl results in an energetic reaction, completed by 5-10 min. at 60-70°
and conen. in vacuo gave a residue of $RCCl:NP(O)(OR')_2$: (R, R' shown, resp.)
Ph, Me, 100%, viscous oil; $p-O_2NC_6H_4$, Me, 100%, m. 107-10°; $m-O_2NC_6H_4$, Me,
89.6%, m. 20-5°; $3,5-(O_2N)_2C_6H_3$, Me, 95.5%, m. 125-7°; $p-ClC_6H_4$, Me, 99%,
liquid. The diphenoxy analogs were prepd. similarly but at 100-5° and were
induced to crystallize by rubbing with petr. ether: Ph, Ph, (I)
42.5%, m. 74-6°; $p-O_2NC_6H_4$, Ph, 83.5%, m. 87-9°; $m-O_2NC_6H_4$, Ph, 81.7%, m.
127-9°; $3,5-(O_2N)_2C_6H_3$, Ph, 61.6%, m. 115-8°; $p-ClC_6H_4$, Ph, 100%, m. 55-7°;
the following were prepd. by heating to 110-20°: Ph, $p-ClC_6H_4$, 35.4%, m.
69-71°; $p-O_2NC_6H_4$, $p-ClC_6H_4$, 92.3%, m. 150-2°; $p-ClC_6H_4$, $p-ClC_6H_4$, 69.7%,
m. 109-11°; Ph, $p-O_2NC_6H_4$ (II) 95.7%, m. 157-60°; $p-O_2NC_6H_4$, $p-O_2NC_6H_4$, 80%,
m. 161-3°; $p-ClC_6H_4$, $p-O_2NC_6H_4$, 89%, m. 137-9°. Heating the tri-Ph deriv.
to 230-40° at 20 mm. gave 90% PhCN and a residue which with NH_4OH gave
$(PhO)_2PONH_2$. Similarly I gave $m-O_2NC_6H_4CN$ and $(PhO)_2POCl$; the prior reaction
rate II gave PhCN and $(p-O_2NC_6H_4O)_2POCl$ which gave the free acid,
m. 174-6° on treatment with 2N NaOH and acidification. The acyls described
above hydrolyzed completely in 2-2.5 hrs. in H_2O yielding 96-9% $RCONHPO(OR')_2$

Organophosphorus

Fluorine-containing trichlorophosphazosulfonaryls and their derivatives.
L. M. Yagupol'skii and V. I. Troitskaya (Inst. Org. Chem., Acad. Sci., Kiev).
Zhur. Obshchei Khim. 29, 552-6 (1959). cf. Kirsanov, this J. 22, 269(1952).
also cf. Olah and Pavlath, Acta chim. Acad. Sci. Hung., 4, 115 (1954).
Heating 0.1 mole p-$FC_6H_4SO_2NH_2$ with 0.103 mole PCl_5 at 105-8° 1.5 hrs. gave
after removal of excess PCl_5 in vacuo and cooling, 99% p-$FC_6H_4SO_2N:PCl_3$, m.
72-3° (from petr. ether). This heated with equimolar amt. of HCO_2H in C_6H_6
to 85° then left overnight gave 96.4% p-$FC_6H_4\overset{SO_2}{N}POCl_2$ (X), m. 135-6° (from C_6H_6),
while repetition of the process (1.5 hr. at 80-5°) gave 86.5% p-$FC_6H_4\overset{SO_2}{N}P(O)-$
(OH)Cl, m. 123-4° (from C_6H_6). Heating 0.01 mole X and 0.01 mole HCO_2H in
10 ml. C_6H_6 1.5 hrs. at 80-5°, addn. of 0.01 mole HCO_2H and heating 4 hrs.
longer gave on cooling 39% p-$FC_6H_4\overset{SO_2}{N}PO(OH)_2$, m. 148-9°. Stirring 29.2 g.
$PhCF_3$ and 25 g. 62% oleum 2 hrs. at 0°, keeping 1 day at room temp. and quen-
ching in satd. NaCl at 0° gave 88.2% crude product of m-$F_3CC_6H_4SO_3Na$; this
with PCl_5 gave 65% m-$F_3CC_6H_4SO_2Cl$, b_6 88-90°, which with NH_3 in C_6H_6 gave 88%
amide, m. 121-2°. This with PCl_5 as above gave 99% m-$F_3CC_6H_4SO_2N:PCl_3$, m.
52-4° (from petr. ether); this gave, as above, m-$F_3CC_6H_4SO_2NPOCl_2$, 84.5%,
m. 82-3°, and m-$F_3CC_6H_4SO_2NPO(OH)_2$, m. 135-6°, this being prepd. best by
keeping the trichloride in a vessel over H_2O 1 week. Treatment of the tri-
chlorides with RONa in ROH at 0-5°, finally 0.5 hr. at room temp. gave after
extn. with H_2O and acidification of the aq. ext., a ppt. of the di-ester, and
the org. layer on evapn. gave the triesters shown below: $AC_6H_4SO_2N:P(OR)_3$
(A and R shown resp.): p-F, Me, 36.3%, m. 45-6°(from C_6H_6-petr. ether); p-F,
Et, 65.2%, b_{10} 202-4°; p-F, Ph, 23.8%, m. 69-70° (from aq. EtOH); p-F, p-
FC_6H_4, 37.2%, m. 70-2° (from aq. EtOH); p-F, p-ClC_6H_4, 53.5%, m. 115-16°;
p-F, p-$O_2NC_6H_4$, 80%, m. 180-1° (from C_6H_6); m-CF_3, Me, 59%, m. 58-60°;
m-CF_3, Et, 85.8%, b_7 185-7°; m-CF_3, p-$O_2NC_6H_4$, 84.2%, m. 167-8°; $AC_6H_4SO_2NH-$
$PO(OR)_2$: p-F, Me, 66.5%, m. 145-6° (from C_6H_6); p-F, Et, 80.8%, m. 118-19°;
p-F, Ph, 12.7%, m. 183-4°; p-F, p-FC_6H_4, 14.2%, m. 142-3°; p-F, p-ClC_6H_4, 6.2%,
m. 149-50° (the above 3 compds. were isolated from the prepn. of tri-esters
above); p-F, p-$O_2NC_6H_4$, 88.6%, m. 177-8°; m-CF_3, Me, 22.5%, m. 93-4°; m-CF_3,

Et, 91.3%, m. 71-3°; m-CF$_3$, p-O$_2$NC$_6$H$_4$, 88%, m. 194-5°. The di-esters above
were best prepd. from the trichloride and 4.5 moles RONa in ROH; the esters
of phenols were prepd. best by addn. of 6 g.at. Na in C$_6$H$_6$ to the trichloride
followed by 6 moles ArOH in dioxane and refluxing until all Na had reacted
after which the soln. was added to 2 moles trichloride in C$_6$H$_6$ at 20° and
was kept 1 hr. The nitrophenol derivs. were prepd. from the Na salt of the
phenol in dry C$_6$H$_6$; this yielded the triaryloxy esters, which saponified
with aq. alc. Na$_2$CO$_3$ (followed by acidification) to the di-esters shown
above. A slight insecticidal activity was found in p-FC$_6$H$_4$SO$_2$N:P(OMe)$_3$ and
the m-CF$_3$ analog.

Phenyldichlorophosphasesulfonaryls. *Organophosphorus*

V. I. Shevchenko and Zh. V. Merkulova (Metallurg. Inst., Dnepropetrovsk).
Zhur. Obshchei Khim. 29, 1005-8 (1959). cf. Kirsanov, this J. 27, 1253 (1957).
Heating an equimolar mixt. of $PhPCl_4$ and $ArSO_2NH_2$ to 70-5° (or higher,
depending on the m.p. of the amide) 15-20 min. results in loss of HCl,
whose removal is then facilitated by blowing with dry CO_2. The residual
solid or oily $ArSO_2N:PPhCl_2$ was rubbed with dry Et_2O and chilled, to
produce the crystalline products, which may be recrystallised from Et_2O
or EtOAc. The following list describes unrecrystallized products, since
the recrystn. raises the m.pt. only slightly and the crude products are
already quite pure: (Ar shown): Ph, 80%, m. 47-9°; o-tolyl, 101%, oil;
p-tolyl, 101.5%, oil; $p\text{-}ClC_6H_4$, 102%, oil; $o\text{-}O_2NC_6H_4$, 92.5%, m. 73-5°;
$m\text{-}O_2NC_6H_4$, 92%, m. 99-100°; $p\text{-}O_2NC_6H_4$, 90%, m. 171-4°; $1\text{-}C_{10}H_7$, 82%,
m. 99-102°; $2\text{-}C_{10}H_7$, 101.2%, resinous solid. The products may be prepd.
also by addn. of an equimolar amount of $ArSO_2NNaCl$ to $PhPCl_2$ in C_6H_6;
the solvent is necessary to moderate the reaction. Addn. of the $PhSO_2$-
$N:PPhCl_2$ to 3 moles MeONa in $MeOH\text{-}C_6H_6$, heating 0.5 hr. at 50°, followed
by removal of the solvents in vacuo, and treatment with H_2O and dil. HCl,
whereupon $PhSO_2NHP(O)PhOMe$, m. 172-3°, is formed in 75% yield.